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Solvent- and Ligand-free Diboration of Alkynes and Alkenes Catalyzed by Platinum Nanoparticles on Titania

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Dedication ((optional))

Platinum nanoparticles supported on titania have shown to efficiently catalyze the diboration of alkynes and alkenes under solvent- and ligand-free conditions in air. The *cis*-1,2-diborylalkenes and 1,2-diborylalkanes were obtained in moderate-to-excellent yields following, in most cases, a simple filtration work-up protocol. The versatility of the *cis*-1,2-diboronvinyl compounds was demonstrated in a series of organic transformations, including the Suzuki-Miyaura cross coupling and the boron-halogen exchange.

Introduction

Boronic acids and their derivatives are versatile and useful starting materials for the formation of carbon-carbon and carbon-heteroatom bonds.[1] Their pivotal role in modern synthetic chemistry has led to the development of new and more efficient methodologies for the preparation of this type of compounds. Among them, the transition-metal catalyzed diboration of carbon-carbon multiple bonds represents an straightforward and atom-economy strategy for this purpose.[2] Particularly interesting is the platinum-catalyzed [$Pt(PPh_3)_4$] addition of bis(pinacolato)diboron (B_2pin_2) to alkynes, pioneered by Miyaura et al., which leads to 1,2-diboronvinyl compounds in a *cis*-selective manner.[3] The utility of the latter was elegantly exemplified by Armstrong et al. in the synthesis of tamoxifen derivatives.[4] Some other methodologies, also involving phosphine-based platinum complexes, were later reported by the groups of Marder[5] and Smith III.[6] Although the catalytic diboration of alkynes is clearly dominated by platinum homogeneous catalysis,[2] the heterogeneous version of this reaction has been mainly studied with other metals, namely: (a) the Pd/C-catalyzed alkyne diboration with [2]borametalloarenophanes to form *ansa*-bis(boryl)alkenes[7] and (b) the alkyne diboration catalyzed by nanoporous gold.[8]

To the best of our knowledge, only Corma and García et al. have studied the heterogeneous platinum-catalyzed diboration of alkynes with B_2pin_2, using for this purpose magnesia-supported platinum nanoparticles.[9] However, some of the aforementioned methodologies suffer from disadvantages such as long reaction times or the necessity of inert atmospheres, phosphane ligands and organic solvents such as DMF, toluene or benzene. The Pt/MgO catalyst could work in some cases in the absence of PPh_3; however, elevated temperatures were required (130-160 ^oC) and the substrate scope covered was rather limited (4 alkynes bearing no functional group).[9] Another common feature of some the above commented catalysts, such as $Pt(PPh_3)_4$[3] and Pt/MgO,[9] is that they are not suitable for alkene diboration.

The first platinum-catalyzed diboration of aliphatic and aromatic terminal alkenes, and some cyclic alkenes was independently achieved by the groups of Miyaura and Smith III, using $Pt(dba)_2$ and $Pt(COD)_2$ [or Pt(NBE)], respectively, as catalysts.[10] Soon after, Marder et al. developed an asymmetric version of this reaction with chiral diborane compounds and $Pt(dba)_2$.[11a] Alkene diboration has also been accomplished with metals other than platinum, such as gold,[12] rhodium,[13] palladium,[14] and copper.[15] The group of Fernández introduced the diboration of alkenes catalyzed by gold(0) nanoparticles[16] and, more recently, an organocatalytic version of this reaction.[17] However, the heterogeneous nature of the gold-nanoparticle process was not clearly ascertained because of the presence of BINAP as ligand. In view of the above information, we can state that the heterogeneous ligand-free catalytic diboration of alkenes has not been described hitherto. Therefore, we can conclude that the information on the heterogeneous platinum-catalyzed diboration of alkynes and alkenes is sparse and that new platinum catalysts which can upgrade the catalytic behaviour of those already reported are welcome.

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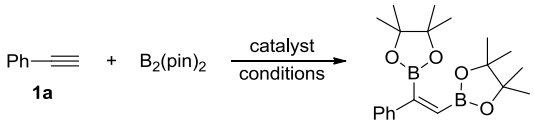
Due to our dedication to studying and understanding the reactivity of active metals and nanoparticles,[18] we have reported the hydrogen-transfer reduction of ketones catalyzed by highly reusable platinum nanoparticles on carbon.[19] More recently, we demonstrated that platinum nanoparticles on titania catalyzed the hydrosilylation of terminal and internal alkynes,[20a] as well as that of diynes.[20b] As part of our research on organic reactions promoted by platinum nanoparticles, we wish to present herein the results attained on the selective diboration of alkynes and alkenes catalyzed by Pt/TiO_2 under solvent- and ligand-free conditions.

Results and Discussion

Screening of the catalysts

The platinum catalysts were prepared by the impregnation method (see the Experimental Section). The diboration of phenylacetylene (**1a**) with bis(pinacolato)diboron [$B_2(bpin)_2$] was used as the model reaction at 70 ºC (Table 1). Initial experiments with Pt/TiO_2 (1 wt.%) in different solvents under argon were unsuccessful (Table 1, entries 1-4). However, the reaction in toluene under air gave the product **2a** in 84% conversion (Table 1, entry 5). It is noteworthy that an excellent conversion was recorded in the absence of solvent under air, whereas the inert atmosphere exerted a deleterious effect on the conversion (Table 1, compare entries 6 and 7). Other supported monometallic catalysts, such as Pt/CeO_2 and Pt/C exhibited a moderate activity under air and solvent-free conditions (Table 1, entries 8 and 9), with Pt/Al_2O_3 performing significantly better under air than under argon atmospheres (Table 1, entries 10 and 11). In contrast, rather poor results were obtained with Pt/zeolite-Y catalysts (Table 1, entry 12). Then, we tested bimetallic Pt-Pd and Pt-Sn catalysts supported on titania; in general, the 1:1 Pt-Sn catalysts behaved better that the 1:1 Pt-Pd counterparts, especially when the processes were carried out in the absence of solvent in air with lower catalyst loading (Table 1, compare entries 13-16 with 17 and 18). A high conversion, comparable to that of Pt/Al_2O_3 was reached with $Pt\text{-}Sn/TiO_2$ in toluene under argon (Table 1, entry 19). Unfortunately, catalyst recycling was troublesome irrespective of the catalyst tested (Table 1, entries 7, 11, and 19). In view of the above results and since solvent-free organic synthesis is one of the most promising steps toward waste prevention and environmental protection,[21] Pt/TiO_2 (1 wt.%) was considered as the catalyst of choice in the absence of solvent and in air (Table 1, entry 7).

Table 1. Catalyst screening in the diboration of phenylacetylene.[a]



2a

Entry	Catalyst (wt.% Pt)	Solvent	Atmosphere	Conversion (%)[b]
1	Pt/TiO_2 (1)	THF	Ar	3
2	Pt/TiO_2 (1)	CH_2Cl_2	Ar	-
3	Pt/TiO_2 (1)	MeCN	Ar	3
4	Pt/TiO_2 (1)	PhMe	Ar	11
5	Pt/TiO_2 (1)	PhMe	air	84
6	Pt/TiO_2 (1)	neat	Ar	13
7	Pt/TiO_2 (1)	neat	air	94 (11)[c]
8	Pt/CeO_2 (1)	neat	air	67
9	Pt/C (1.5)	neat	air	60
10	Pt/Al_2O_3 (1)	neat	Ar	53
11	Pt/Al_2O_3 (1)	neat	air	87 (44)[c]
12	Pt/zeolite-Y (1)	neat	air	1 (3)[d]
13	$Pt\text{-}Pd/TiO_2$ (1)	neat	air	50
14	$Pt\text{-}Pd/TiO_2$ (1)[e]	neat	air	62
15	$Pt\text{-}Sn/TiO_2$ (2)	neat	Ar	14
16	$Pt\text{-}Sn/TiO_2$ (2)	neat	air	35
17	$Pt\text{-}Sn/TiO_2$ (1)	neat	air	75
18	$Pt\text{-}Sn/TiO_2$ (1.5)	neat	air	74
19	$Pt\text{-}Sn/TiO_2$ (2)[f]	PhMe	Ar	88 (0)[c]

[a] Reaction conditions: **1a** (0.5 mmol), $B_2(pin)_2$ (0.5 mmol), catalyst (20.0 mg), solvent (2.0 mL) or neat, 70 ºC, 18 h. [b] Conversion determined by GLC. [c] Conversion in a second cycle. [d] Conversion using the non-calcined catalyst. [e] 40.0 mg of catalyst were used. [f] Catalyst reduced at 250 ºC

Characterization of the Pt/TiO_2 catalyst

The Pt/TiO_2 catalyst was calcined in air at 400 ºC for 2 h after preparation (see the Experimental Section). TEM analysis[20b] shows that it is composed of very small (1-2 nm) platinum clusters with a narrow size distribution, homogeneously dispersed on the surface of the titania crystals (Supporting Information). The XPS spectrum in the Pt 4*f* region for this catalyst is shown in Figure 1. It can be deconvoluted into four peaks, two of them (those placed at lower binding energies) corresponding to the Pt $4f_{7/2}$ level and the others to the Pt $4f_{5/2}$ level. The peaks arising from the Pt $4f_{7/2}$ level are centered at 73.0 and 74.8 eV, which can be assigned to oxidized platinum species. An accurate assignment of the peaks is not easy, as the binding energies of the core electrons are affected not only by the metal oxidation state but also by the surrounding atoms. The binding energy of the Pt $4f_{7/2}$ level for Pt(IV) coordinated to six chlorine atoms (as in the H_2PtCl_6 precursor compound) is reported to be 75.3 eV (for K_2PtCl_6), but it decreases to 74.8 eV for PtO_2 and to 74.2 eV for $Pt(OH)_4$. Additionally, the Pt $4f_{7/2}$ level for $PtCl_2$ is about 73.4 eV, whereas that for $Pt(OH)_2$ is about 72.4 eV.[22] In this way, the XPS spectrum of the catalyst reveals that it contains two different kinds of Pt(II) species, although the presence of some remaining Pt(IV) cannot be discarded. This indicates, on one side, that reductive decomposition of the metal precursor has taken place upon impregnation, by which the parent Pt(IV) is reduced to Pt(II). On the other hand, this surface decomposition is accompanied by dechlorination to a large extent. In fact, the XPS atomic Cl/Pt ratio is as low as 0.6 in the catalyst, whereas it is 6 in the parent precursor. One important observation is that XPS analysis indicates the absence of Pt(0) species (binding energy at around 70-71 eV). Therefore, we can conclude that the catalyst is mainly composed of Pt(II) in the form of PtO and $PtCl_2$ (the latter in minor proportion) together with some Pt(IV), primarily, as PtO_2.

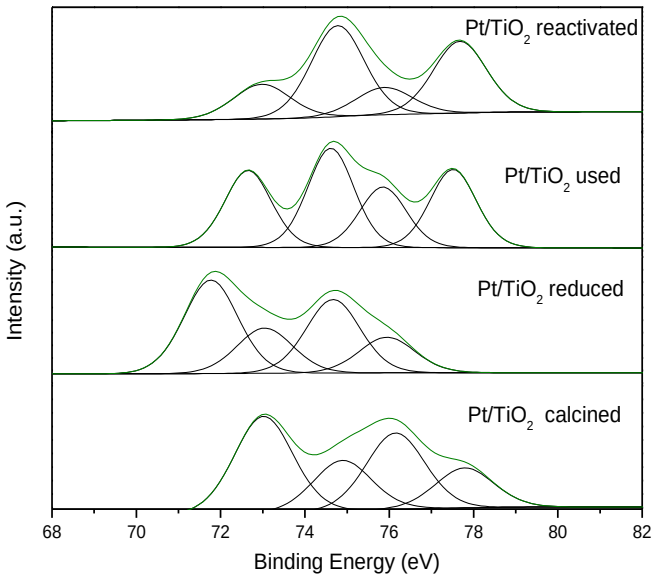


Figure 1. XPS spectra for the Pt 4f region.

Table 2 reports the surface atomic ratios for Pt/TiO_2 after different treatments, as determined by XPS. When one compares the fresh calcined catalyst with the used one, a strong decrease in the Pt/Ti ratio is clearly observed (Table 2, entries 1 and 3). This indicates a loss of surface platinum, which could be due to metal sintering. However, the mild reaction conditions applied allows discarding this possibility. This assertion is also supported by the TEM images of the used catalyst, which show that no modification has taken place in the particle size distribution after reaction (Supporting Information). The possibility of platinum leaching was also ruled out as the amount of platinum found by ICP-MS analysis of the reaction filtrate was as low as 0.75 ppb. The third, most likely possibility, is the coverage of surface platinum by reaction species.

Table 2. Surface atomic ratios from XPS analysis.

Entry	Catalyst	Pt/Ti	O/Ti	Cl/Pt
1	Pt/TiO_2 (calcined)	0.035	3.706	0.622
2	Pt/TiO_2 (reduced)	0.029	3.693	0.541
3	Pt/TiO_2 (used)	0.013	4.203	0.007
4	Pt/TiO_2 (reactivated)	0.009	3.829	0.007

The distribution of the platinum species clearly changes during the reaction, as can be deduced when the XPS spectra for Pt 4f region of the calcined and used catalysts are compared (Figure 1). It is clear that the proportion of high-valent platinum (appearing at higher binding energies) is increased upon reaction. Given the low amount of chlorine in this sample (Table 2, entry 3), these species are likely to correspond to PtO_2 and/or to Pt coordinated to electron-withdrawing species (e.g., organoboron compounds). The noticeable nearly complete dechlorination of the catalyst upon reaction (Cl/Ti atomic ratio varies from 0.0622 to 0.007) would indicate that the chloride ligands are being removed during the reaction (Table 2, entries 1 and 3).

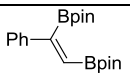
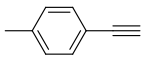
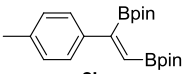
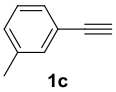
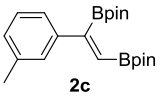
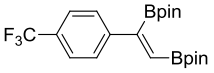
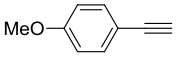
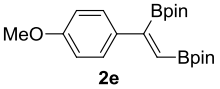
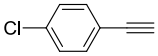
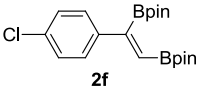
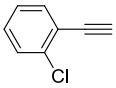
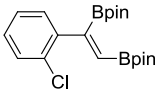
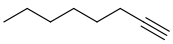
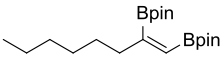
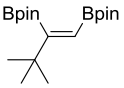
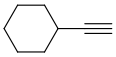
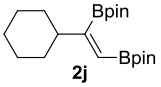
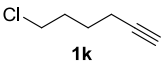
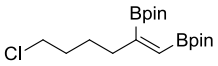
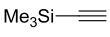
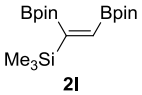
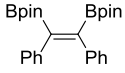
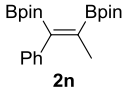
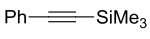
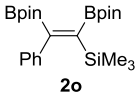
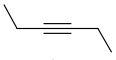
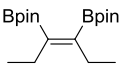
With the aim of answering some of the posed questions, the used catalyst was subjected to a calcination treatment in air, at 400 ºC for 4 h. The objective was to remove any of the reaction products that could cover the platinum surface. It can be seen in Table 2 that the atomic ratios were nearly unmodified. Furthermore, the XPS spectra (Figure 1) shows that the relative amount of high-valent platinum has increased, which can be explained by a larger amount of PtO_2 species as a result of the calcination treatment. It has to be noted that this reactivation treatment allowed increasing to some extent the catalytic activity. Thus, the conversion attained with the fresh calcined catalyst (94%, Table 1, entry 7) decreased up to 11% in a second cycle (without any reactivation treatment). The conversion increased up to 33% after calcination in air. Thus, it can be concluded that the reactivation treatment could effectively remove reaction products that were covering the platinum active sites, but it also decreased the amount of Pt(II) species, which seems to be important for this reaction.

Finally, in order to add some light on which are the active species for this reaction, the Pt/TiO_2 catalyst was also tested after a reduction treatment. Thus, the calcined Pt/TiO_2 catalyst was subjected to a reduction treatment under a H_2 flow (50 mL/min) at 250 ºC for 2 h. TEM images show that there is not any clear modification of the particle size distribution (Supporting Information). The XPS spectra (Figure 1) brings into view that platinum is effectively reduced to the metallic state (band centered at 71.7 eV), although some Pt(II) species are still present (72.8 eV). In this case, there is a slight decrease in the Pt/Ti atomic ratio and also a small dechlorination (Cl/Pt shifts from 0.622 to 0.541, Table 2, entry 2). Reaction with this catalyst was carried out under Ar and compared with that for the calcined catalyst (Table 1, entry 6). Thus, whereas the reaction with calcined Pt/TiO_2 yielded a 13% conversion under these conditions, a conversion degree of only 3% was obtained with the reduced sample. These results would allow to conclude the importance of Pt(II) species as active sites for the reaction instead of reduced Pt(0) species, which are commonly considered in the proposed reaction mechanisms catalyzed either by platinum complexes[3,6,23] or platinum nanoparticles.[9] In these cases, an oxidative addition step of the B-B bond to Pt(0) is always suggested in the catalytic cycle. The absence of metallic platinum and major presence of Pt(II) in our fresh catalyst, together with the notable amount of Pt(IV) observed in the used catalysts, points to an unprecedented Pt(II)/Pt(IV) mechanism which might operate in this catalytic system. However, more experimental studies are needed to confirm this claim.

Diboration of alkynes catalyzed by Pt/TiO_2

The optimized catalyst and reaction conditions [Pt/TiO_2 (1 wt.%) 0.2 mol%, neat, air, 70 ºC] were first applied to the diboration of terminal alkynes (Table 3). The kinetic profile for the diboration of phenylacetylene shows a polynomial increase of the conversion versus time, with the former being quantitative after 11 h (Figure 2). For this particular reaction, TON and TOF of up to 1935 and 176 h^{-1} have been meassured. It is worthwhile mentioning that while the addition of $B_2(pin)_2$ to phenylacetylene catalyzed by $Pt(PPh_3)_4$ (DMF, 80 ºC, 24 h)[3a] or $Pt(NBE)_3$ (PPh_3, PhMe, ambient temperature, 36 h)[5b] was inefficient (≤30% conversion), our catalytic system furnished the corresponding product **2a** in near quantitative yield (Table 3, entry 1). The reaction conditions were equally effective for some other aromatic alkynes bearing electron-neutral, electron-withdrawing, or electron-releasing

Table 3. Diboration of alkynes catalyzed by Pt/TiO_2.[a]

Entry	Alkyne	t (h)	Product	Yield (%)[b]
1	**1a**	16	 **2a**	96
2	 **1b**	16	 **2b**	94
3	 **1c**	16	 **2c**	80[c]
4	 **1d**	16	 **2d**	88[c]
5	 **1e**	16	 **2e**	85[c]
6	 **1f**	16	 **2f**	84
7	 **1g**	16	 **2g**	89
8	 **1h**	24	 **2h**	95
9	 **1i**	16	 **2i**	94
10	 **1j**	16	 **2j**	91
11	 **1k**	18	 **2k**	75
12	 **1l**	12	 **2l**	88
13	**1m**	24	 **2m**	62[c]
14	**1n**	16	 **2n**	92
15	 **1o**	12	 **2o**	82[c]
16	 **1p**	18	 **2p**	85

[a] Reaction conditions: **1a** (0.5 mmol), $B_2(pin)_2$ (0.5 mmol), catalyst (20.0 mg, 0.2 mol%), in air at 70 ºC. [b] Isolated yield after filtration of the reaction crude (Celite and alumina) and washing with hexane. [c] Isolated yield after purification by column chromatography (alumina, hexane/ethyl acetate).

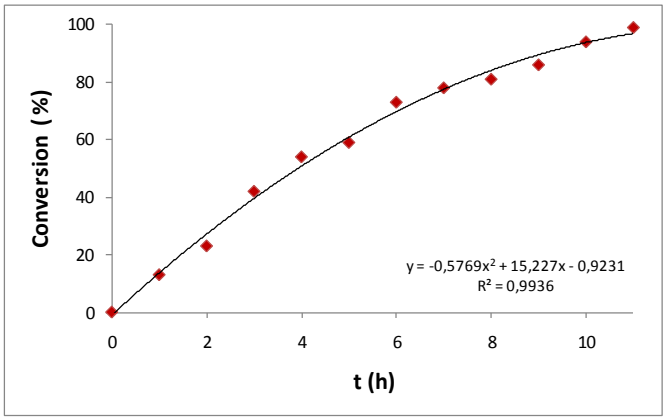


Figure 2. Plot showing the evolution of the diboration of phenylacetylene catalyzed by Pt/TiO_2.

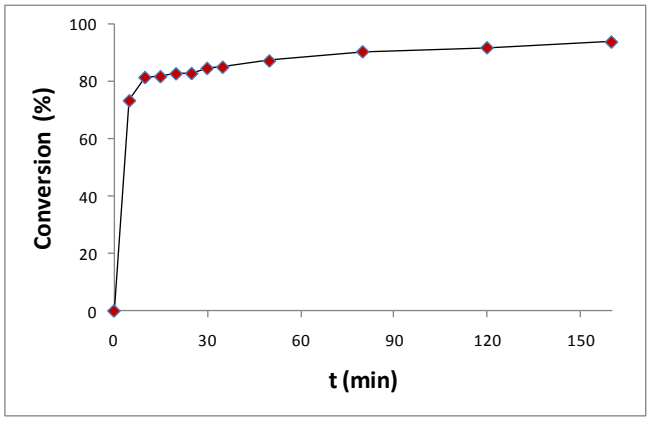


Figure 3. Plot showing the evolution of the diboration of styrene catalyzed by Pt/TiO_2.

groups (Table 3, entries 2-5) as well as for chlorinated aromatics (Table 3, entries 6 and 7). We next studied a range of aliphatic terminal alkynes; linear alkyl (**1h**), branched (**1i**) and cycloalkyl-substituted (**1j**) acetylenes were diborated in high yields (Table 3, entries 8-10). Relatively lower yield was obtained in the case of the functionalized chloroalkyl acetylene **1k** (Table 3, entry 11), whereas higher yield was noted in the case of trimethylsilylacetylene (**1l**) (Table 3, entry 12). Not only terminal but internal alkynes were sucessfully subjected to the stardard conditions. Diphenylacetylene (**1m**) was found to be, comparatively, more reluctant to react, probably because of the steric hindrance developed in the transition state to the product **2m** (Table 3, entry 13). Other internal alkynes including (methyl)phenylacetylene (**1n**), (trimethylsilyl)phenylacetylene (**1o**), or even the aliphatic hex-3-yne (**1p**) gave rise to the expected products **2n**-**2p** in good-to-high isolated yields (Table 3, entries 14-16). It is worth noting that exclusive *cis*-diboration was observed for all the alkynes studied.

Diboration of alkenes catalyzed by Pt/TiO_2

Contrary to the behaviour of other platinum catalysts,[3,9] this methodology could be extended to the diboration of alkenes (Table 3). Styrene (**3a**) was found to react much faster than phenylacetylene (**2a**), reaching 82% conversion in only 10 min and almost quantitative conversion after 2 h (Figure 3) (Table 3, entry 1). The halogenated styrenes **3b** and **3c** were successfully diborated in good-to-high yields though required longer heating (Table 3, entries 2 and 3). The reactions were somewhat sluggish in the case of the cyclic olefins **3d** and **3e**, producing the *cis* diborated compounds **4d** and **4e**, respectively, in moderate yields (Table 3, entries 4 and 5). Nevertheless, the latter results were much better that those achieved with $Pt(dba)_2$ in toluene for these cyclic olefins, where diboration was unsuccessful.[10a] The lower yield could be attributed to the steric hindrance arisen because of the presence of two Bpin units in a *cis* disposition. Unlike cyclic olefins, terminal alkene oct-1-ene (**3f**) nicely underwent diboration, giving the 1,2-diboron alkane in good yield (Table 3, entry 6). In this case, we must highlight that no isomers were formed resulting from β-hydride elimination processes. Two vinyl silanes were subjected to the standard reaction conditions, with triethoxy(vinyl)silane (**3h**) leading to the expected product **4h** in higher yield that **4g**, derived from trimethyl(vinyl)silane (**3g**) (Table 3, entries 7 and 8). A different trend was observed for the α,β-unsaturated ester ethyl cinnamate (**3i**) which, as expected, gave the β-mono-borated product, probably following a 1,4-addition/hydrolysis sequence (Table 3, entry 9).[24]

An advantageous feature of this methodology is that, in most cases of alkyne and alkene diboration, the reaction crudes were pure enough to make purification by chromatographic methods unnecessary; products could be obtained after simple filtration and solvent evaporation.

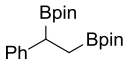
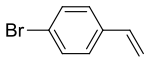
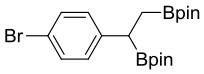
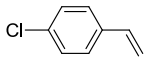
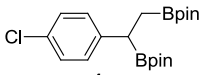
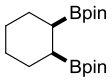
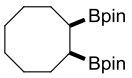
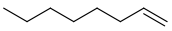
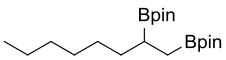
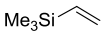
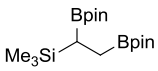
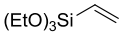
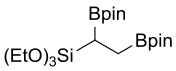
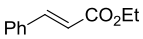
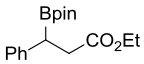
Chemical transformations of the *cis*-1,2-diborylalkenes

The versatility of the 1,2-diboronvinyl compounds was demonstrated in a series of organic transformations, including the Suzuki-Miyaura cross coupling and the boron-halogen exchange (Scheme 1). When compound **2a** was reacted with iodobenzene under standard Suzuki-Miyaura conditions,[4] 1,1,2-triphenylethene (**5**) was obtained in quantitative yield. Treatment of **2a** with iodine under basic conditions furnished the α-boron-β-iodo styrene derivative **6** in short reaction time and excellent yield. The β-chloro (**7**) and β-bromo (**8**) analogues were readily synthesized by reaction of **2a** with the corresponding copper(II) halides in aqueous THF. All these α-boron-β-halo styrenes, which were obtained with retention of the stereochemistry, are new valuable compounds which might be further used in coupling reactions. Oxidation of the bromo derivative **8** led to α-bromoacetophenone (**9**) in good yield.

Conclusion

A variety of monometallic and bimetallic platinum-based supported catalysts have been tested in the diboration of phenylacetylene. The catalyst consisting of platinum nanoparticles on titania exhibited the best performance under solvent- and ligand-free conditions in air. This methodology has been successfully applied to the diboration of a wide range of alkynes, including terminal aryl and alkyl acetylenes as well as internal alkynes, in all cases with exclusive *cis* diastereoselectivity. Interestingly, not only alkynes but alkenes could be diborated under the same simple reaction conditions. In general, products are obtained in good-to-excellent isolated yields. XPS data of different catalyst samples suggest the participation of Pt(II)/Pt(IV) species in the catalytic cycle. The fact that reactions proceed in the absence of solvent and ligand under air, together with the generally applied easy purification procedure and low catalyst

Table 4. Diboration of alkenes catalyzed by Pt/TiO_2.[a]

Entry	Alkene	t (h)	Product	Yield (%)[b]
1	 **3a**	2	 **4a**	92
2	 **3b**	16	 **4b**	81[c]
3	 **3c**	16	 **4c**	90
4	 **3d**	24	 **4d**	46[c]
5	 **3e**	24	 **4e**	55
6	 **3f**	24	 **4f**	82
7	 **3g**	12	 **4g**	65
8	 **3h**	12	 **4h**	85
9	 **3i**	18	 **4i**	73[c]

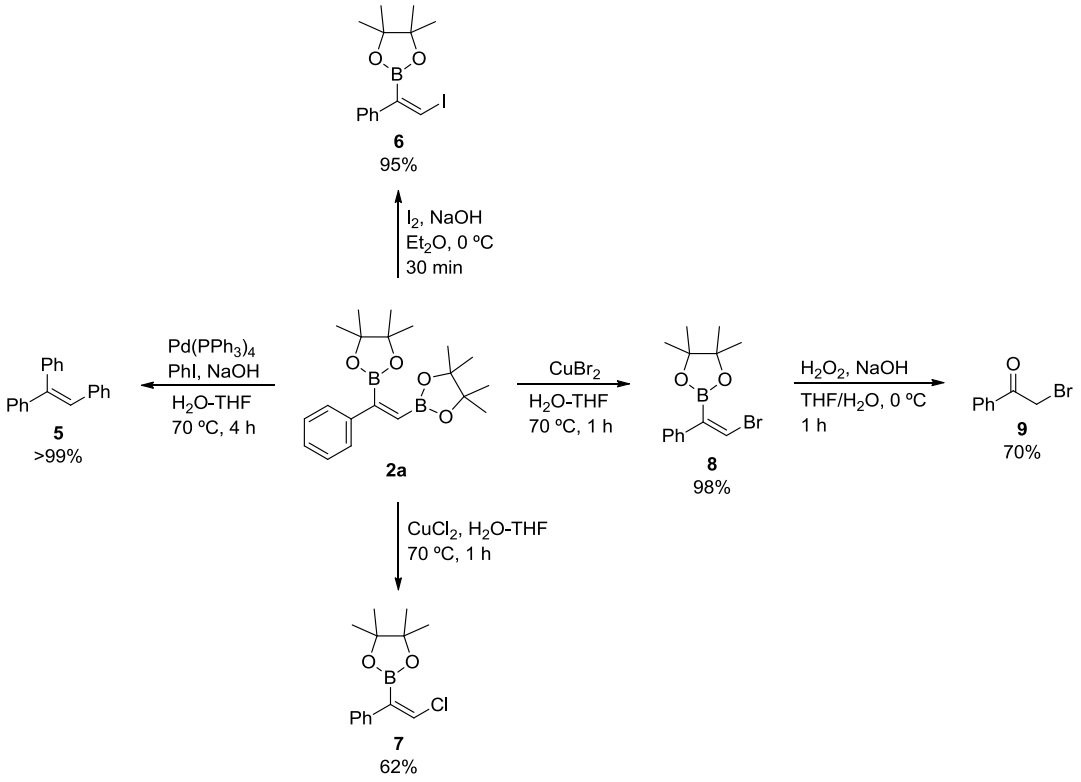
[a] Reaction conditions: **1a** (0.5 mmol), $B_2(pin)_2$ (0.5 mmol), catalyst (20.0 mg, 0.2 mol%), in air at 70 ºC. [b] Isolated yield after filtration of the reaction crude (Celite and alumina) and washing with hexane. [c] Isolated yield after purification by column chromatography (alumina, hexane/ethyl acetate).

loading, makes this an environmentally benign approach to the synthesis of diboron compounds. Moreover, taking additionally into account that the processes are highly stereoselective with 100% atom economy, it would be quite reasonable to include them within the set of reactions belonging to the so-called click chemistry.[25] Finally, we have also presented some interesting chemical transformations of a *cis*-1,2-diboronvinyl derivative, including Suzuki-Miyaura and boron-halogen exchange reactions.

Experimental Section

General: Degussa P25 TiO_2 (60% anatase, 40% rutile) with a surface area of 50 m^2g^{-1} (N_2, –195 ºC, BET method) was used as support, after being calcined in air at 500 ºC for 5 h. X-ray photoelectron spectra (XPS) were acquired with a VG-Microtech Multilab 3000 spectrometer equipped with a hemispherical electron analyzer and a Mg Kα (*h* = 1253.6 eV, 1 eV = 1.602 × 10^{-19} J) 300 W X-ray source. Conventional TEM analysis was carried out with a Jeol model JEM-210 electron microscope working at 200 kV and equipped with a INCA Energy TEM 100 analytical system and a SIS Mega View II camera. Samples for analysis were suspended in methanol and placed on copper grids with a holey carbon film support.

All reagents were of the best grade commercially available and were used without further purification. All reactions were carried out without air exclusion on a multireactor apparatus using the corresponding reactor tubes. Melting points were measured with a Reichert Thermovar apparatus and are uncorrected. NMR spectra were recorded on Bruker Avance 300, 400, and 500 spectrometers (300 and 400 MHz for ^{1}H NMR; 75 and 101 MHz for ^{13}C NMR; 160 MHz for ^{11}B NMR) using $CDCl_3$ as solvent and TMS as internal standard; chemical shifts are given in (δ) parts per million and coupling constants (*J*) in Hertz. Infrared analysis was performed with a Jasco 4100LE (Pike MIRacle ATR) spectrophotometer; wavenumbers are given in cm^{-1}. Mass spectra (EI) were obtained at 70 eV on an Agilent 5973 spectrometer; fragment ions in *m/z* with relative intensities (%) in parenthesis. HRMS analyses were also carried out in the electron impact mode (EI) at 70 eV on a Finnigan MAT95S spectrometer. Elemental analyses were carried out on a Thermo Finnigan Flash 1112 microanalyzer. The purity of volatile compounds and the chromatographic analyses (GLC) were determined with a Hewlett Packard HP-6890 instrument equipped with a flame ionization detector and a 30 m capillary column (0.32 mm diameter, 0.25 μm film thickness), using nitrogen (2 mL/min) as carrier gas, $T_{injector}$ = 270 ºC, T_{column} = 60 ºC (3 min) and 60–270 ºC (15 ºC/min); retention times (t_r) are given in min. Thin layer chromatography was carried out on silica gel pre-coated aluminum sheets (Macherey-



Scheme 1. Chemical transformations of *cis*-1,2-diborylalkene **2a**.

Nagel). Column chromatography was performed using silica gel 60 of 40–60 microns (hexane/EtOAc as eluent).

It is noteworthy that the carbon atoms attached to boron were not observed in the ^{13}C NMR spectra of the new compounds characterized below. It is often the case that these signals are very broad and cannot be detected.

Typical Procedure for the Preparation of Pt/TiO_2: [26] The Pt/TiO_2 catalyst was prepared by the impregnation method with an aqueous solution of $H_2PtCl_6{\cdot}6H_2O$ (Aldrich) of the appropriate concentration to achieve a Pt content of 1 wt.%. The slurry (10 mLg^{-1} of TiO_2) was stirred for 12 h and the excess of solvent was removed by heating at 90 ºC under vacuum in a rotary evaporator. Finally, the catalyst was dried at 110 ºC for 24 h and calcined at 400 ºC for 5 h, with a heating rate of 3 ºC min^{-1}.

General procedure for the diboration reaction: The alkyne or alkene (0.5 mmol), $B_2(pin)_2$ (0.5 mmol, 127.0 mg), and the catalyst (Pt/TiO_2, 20.0 mg, 0.2 mol%) were stirred during the specified time at 70 ºC (see Tables 3 and 4). The progress of the reaction was monitored by TLC and GLC until total or steady conversion was achieved. The resulting mixture was dissolved in hexane (20.0 mL) followed by the addition of basic alumina and removal of the solvent in vacuo. The reaction crude absorbed on alumina was subjected to column chromatography (basic alumina, hexane/EtOAc) to give the pure borylated compounds **2** or **4**. In the cases where the reaction was complete (see Tables 2 and 3), the mixture was filtered through a pad containing Celite and alumina and washed with hexane giving, after solvent evaporation, the expected products without any further purification. Compounds **2a**,[3b] **2b**,[27] **2d**,[28] **2e**,[5b] **2h**,[3a] **2i**,[27] **2j**,[3a] **2m**,[3a] **2n**,[4] **2p**,[4] **4a**,[5b] **4d**,[17] **4e**,[13b] **4f**,[17] and **4i**[29] were characterized by comparison of their physical and spectroscopic data with those reported in the literature. Data for the new compounds follow:

(*E*)-2,2'-[1-(*m*-Tolyl)ethene-1,2-diyl]bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (2c): Yellow oil; t_r 16.99; R_f 0.88 (hexane/EtOAc 9.5:0.5); IR ν 2976, 2950, 1600, 1371, 1332, 1332, 1314, 1139. 969. 851, 838 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 1.30 (s, 12H), 1.38 (s, 12H), 2.32 (s, 3H), 6.27 (s, 1H), 7.05–7.08 (m, 1H), 7.18–7.21 (m, 2H), 7.23–7.25 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 21.6, 25.0, 25.2, 83.7, 84.2, 123.8, 127.5, 128.3, 128.5, 137.9, 143.2; ^{11}B NMR (160 MHz, $CDCl_3$) δ 31.21; MS *m/z* 370 (M^+, 0.1), 281 (29), 253 (10), 228 (12), 209 (10), 208 (18), 207 (100), 96 (11), 84 (48). Elemental analysis calcd. for $C_{21}H_{32}B_2O_4$: C 68.15, H 8.72; Found: C 68.48, H 8.92.

(*E*)-2,2'-[1-(4-Chlorophenyl)ethene-1,2-diyl]bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (2f): Yellow oil; t_r 17.69; R_f 0.73 (hexane/EtOAc 9.5:0.5); IR ν 3040, 2977, 2932, 1596, 1488, 1378, 1372, 1332, 1316, 1214, 1138, 1091, 968, 849, 834, 822 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 1.31 (s, 12H), 1.37 (s, 12H), 6.27 (s, 1H), 7.27–7.29 (m, 2H), 7.34–7.37 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 25.0, 25.2, 83.9, 84.4, 128.1, 128.6, 133.6, 141.7; ^{11}B NMR (160 MHz, $CDCl_3$) δ 30.97; MS *m/z* 390 (M^+, 6), 334 (12), 333 (11), 332 (14), 251 (36), 250 (29), 249 (100), 248 (47), 209 (15), 191 (20), 84 (95), 83 (16), 69 (18), 55 (10). Elemental analysis calcd. for $C_{20}H_{29}B_2ClO_4$: C 61.51, H 7.49; Found: C 61.82, H 7.79.

(*E*)-2,2'-[1-(2-Chlorophenyl)ethene-1,2-diyl]bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (2g): Yellow oil; t_r 16.87; R_f 0.90 (hexane/EtOAc 9.5:0.5); IR ν 3040, 2977, 2932, 1603, 1467, 1387, 1378, 1370, 1319, 1213, 1137, 968, 848, 757, 737, 679 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 1.32 (s, 12H), 1.33 (s, 12H), 6.19 (s, 1H), 7.15–7.21 (m, 2H), 7.22–7.25 (m, 1H), 7.26–7.31 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 25.0, 25.1, 83.8, 84.2, 127.1, 128.4, 129.0, 130.0, 132.2, 144.1; ^{11}B NMR (160 MHz, $CDCl_3$) δ 29.99; MS *m/z* 390 (M^+, 0.5), 334 (19), 333 (16), 332 (13), 251 (38), 250 (29), 249 (100), 248 (46), 191 (20), 190 (11), 129 (29), 128 (13), 84 (75), 83 (16). Elemental analysis calcd. for $C_{20}H_{29}B_2ClO_4$: C 61.51, H 7.49; Found: C 61.91, H 7.78.

(*E*)-2,2'-(6-Chlorohex-1-ene-1,2-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (2k): Pale yellow oil; t_r 15.69; R_f 0.57 (hexane/EtOAc 9.5:0.5); IR ν 2977, 2937, 1618, 1377, 1333, 1306, 1137, 968, 859, 850 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 1.26 (s, 12H), 1.30 (s, 12H), 1.53–1.62 (m, 2H), 1.73–1.81 (m, 2H), 2.25 (td, *J* = 7.6, 1.3 Hz, 2H), 3.52 (t, *J* = 6.7 Hz, 2H), 5.86 (s, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 25.0, 25.1, 25.9, 32.2, 39.9, 45.2, 83.5, 88.9; ^{11}B NMR (160 MHz, $CDCl_3$) δ 30.34; MS *m/z* 370 (M^+, 1), 313 (12), 312 (24), 311 (10), 272 (12), 271 (10), 270 (34), 269 (15), 237 (14), 231 (34), 230 (26), 229 (100), 228 (46), 107 (11), 85 (13), 84 (69), 83 (77), 81 (12), 69 (23), 59 (19), 55 (21). Elemental analysis calcd. for $C_{18}H_{33}B_2ClO_4$: C 58.35, H 8.98; Found: C 58.48, H 9.12.

(*E*)-[1,2-Bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)vinyl)trimethylsilane (2l): Pale yellow semisolid; t_R 13.31; R_f 0.56 (hexane/EtOAc 9.5:0.5); IR ν 2977, 2927, 1584, 1460, 1368, 1329, 1298, 1230, 1138, 970, 934, 857, 837 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 0.10 (s, 9H), 1.26 (s, 12H), 1.33 (s, 12H), 6.59 (s, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ -1.3, 25.1, 25.4, 83.6, 83.7; ^{11}B NMR (160 MHz, $CDCl_3$) δ 33.23; MS *m/z* 352 (M^+, 1), 337 (15), 294 (10), 101 (16), 85 (13), 84 (100), 83 (75), 73 (15), 69 (28), 55 (20). Elemental analysis calcd. for $C_{17}H_{34}B_2O_4Si$: C 57.98, H 9.73; Found: C 58.10, H 9.92.

(*Z*)-Trimethyl[2-phenyl-1,2-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)vinyl]silane (2o): White solid; m.p. 121.0–123.9 ºC; t_r 12.69; R_f 0.56 (hexane/EtOAc 9.5:0.5); IR ν 2977, 2926, 1371, 1304, 1292, 970, 839, 754, 700 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 0.25 (s, 9H), 0.99 (s, 12H), 1.22 (s, 12H), 7.13–7.18 (m, 1H), 7.20–7.23 (m, 4H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 1.1, 25.1, 25.3, 83.4, 83.8, 126.7, 127.6, 127.9, 147.2; ^{11}B NMR (160 MHz, $CDCl_3$) δ 29.85; MS *m/z* 370 (M^+, 1), 313 (12), 312 (24), 311 (10), 272 (12), 271 (10), 270 (34), 269 (15), 237 (14), 231 (34), 230 (26), 229 (100), 228 (46), 107 (11), 85 (13), 84 (69), 83 (77), 81 (12), 69 (23), 59 (19), 55 (21). Elemental analysis calcd. for $C_{23}H_{38}B_2O_4Si$: C 64.51, H 8.94; Found: C 64.72, H 8.82.

2,2'-[1-(4-Bromophenyl)ethane-1,2-diyl]bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (4b): White solid; m.p. 82.5–85.7 ºC; t_r 17.23; R_f 0.68 (hexane/EtOAc 9.5:0.5); IR ν 2977, 2927, 1483, 1370, 1354, 1320, 1138, 1006, 966, 841, 820, 690 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 1.08 (dd, *J* = 16.0, 5.9 Hz, 1H), 1.17 (s, 6H), 1.18 (s, 6H), 1.20 (s, 12H), 1.34 (dd, *J* = 16.0, 10.7 Hz, 1H), 2.48 (dd, *J* = 10.6, 5.9 Hz, 1H), 7.07–7.12 (m, 2H), 7.31–7.36 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 24.6, 24.8, 25.1, 83.3, 83.5, 118.7, 129.9, 131.3, 144.6; ^{11}B NMR (160 MHz, $CDCl_3$) δ 23.67; MS *m/z* 436 (M^+, 1), 297 (21), 296 (13), 295 (23), 294 (11), 84 (100), 83 (24), 69 (13). Elemental analysis calcd. for $C_{20}H_{31}B_2BrO_4$: C 54.97, H 7.15; Found: C 55.12, H 7.36.

2,2'-[1-(4-Chlorophenyl)ethane-1,2-diyl]bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (4c): White solid; m.p. 77.5–80.5 ºC; t_r 17.23; R_f 0.72 (hexane/EtOAc 9.5:0.5); IR ν 2979, 2930, 1486, 1357, 1321, 1263, 1211, 966, 840, 822, 705 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 1.08 (dd, *J* = 16.0, 5.9 Hz, 1H), 1.17 (s, 6H), 1.19 (s, 6H), 1.20 (s, 12H), 1.34 (dd, *J* = 16.0, 10.6 Hz, 1H), 2.50 (dd, *J* = 10.6, 5.9 Hz, 1H), 7.12–7.21 (m, 4H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 24.6, 24.8, 25.1, 83.3, 83.5, 128.3, 129.4, 130.7, 144.1; ^{11}B NMR (160 MHz, $CDCl_3$) δ 22.27; MS *m/z* 392 (M^+, 1), 253 (11), 251 (31), 250 (14), 84 (100), 83 (17), 69 (13). Elemental analysis calcd. for $C_{20}H_{31}B_2ClO_4$: C 61.20, H 7.96; Found: C 61.40, H 8.82.

[1,2-Bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl]trimethylsilane (4g): White solid; m.p. 48.6–52.8 ºC; t_r 13.03; R_f 0.46 (hexane); IR ν 2976, 2927, 1377, 1360, 1339, 1304, 1240, 1140, 1164, 855, 835 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 0.01 (s, 9H), 0.39 (dd, *J* = 12.1, 3.1 Hz, 1H), 0.77 (dd, *J* = 16.3, 3.1 Hz, 1H), 0.89 (dd, *J* = 16.3, 12.1 Hz, 1H), 1.22 (s, 12H), 1.23 (s, 12H); ^{13}C NMR (101 MHz, $CDCl_3$) δ –1.8, 24.8, 24.9, 25.2, 82.7, 83.0; ^{11}B NMR (160 MHz, $CDCl_3$) δ 34.34; MS *m/z* 354 (M^+, 1), 339 (16), 296 (15), 257 (15), 255 (11), 254 (51), 253 (24), 239 (17), 213 (48), 212 (23), 197 (26), 196 (13), 157 (15), 156 (19), 155 (44), 154 (19), 143 (12), 113 (11), 101 (16), 85 (13), 73 (21), 69 (25), 55 (23). Elemental analysis calcd. for $C_{17}H_{36}B_2O_4Si$: C 57.65, H 10.25; Found: C 57.74, H 10.43.

[1,2-Bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl]triethoxysilane (4h): Colourless oil; t_r 14.84; R_f 0.50 (hexane); IR ν 2975, 2926, 2883, 1369, 1343, 1308, 1141, 1103, 1078, 954, 781, 761 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 0.67 (dd, *J* = 10.8, 4.7 Hz, 1H), 1.19–1.26 (m, 35H), 3.83 (q, *J* = 7.0 Hz, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 18.4, 24.5, 24.9, 25.0, 25.2, 58.6, 82.9, 83.1; ^{11}B NMR (160 MHz, $CDCl_3$) δ 34.95; MS *m/z* 444 (M^+, 1), 386 (11), 328 (17), 313 (16), 286 (13), 273 (14), 272 (56), 271 (17), 259 (10), 257 (19), 245 (36), 244 (22), 243 (11), 217 (27), 216 (25), 215 (67), 214 (20), 205 (12), 189 (18), 188 (10), 179 (10) 178 (21), 176 (10), 163 (36), 161 (30), 160 (20), 159 (10), 143 (17), 142 (10), 133 (13), 119 (15), 115 (12), 85 (14), 84 (100), 83 (87), 79 (12), 69 (34), 55 (27). Elemental analysis calcd. for $C_{20}H_{42}B_2O_7Si$: C 54.07, H 9.53; Found: C 54.39, H 9.78.

Suzuki-Miyaura reaction of 2a and iodobenzene: Following a literature procedure,[4] compound **5** was obtained in quantitative yield. Compound **5** was characterized by comparison of its physical and spectroscopic data with those of an authentic commercial sample.

Iodination of compound 2a. Typical procedure:[30] A solution of NaOH (2.0 mL, 3N) was added to the diboron compound **2a** (0.5 mmol, 178.0 mg) dissolved in Et_2O (2.0 mL). The mixture was cooled to 0 ºC and a solution of iodine (304.6 mg, 1.2 mmol) in Et_2O (4.0 mL) was added. The resulting mixture was stirred for 30 min and the reaction crude was washed with a saturated solution of $Na_2S_2O_3$ (2 × 5.0 mL) and water (10.0 mL). The organic phase was extracted with Et_2O (2 × 15.0 mL), dried over $MgSO_4$ and filtrated. The solvent was removed under vacuum giving the product **6** as a yellow oil (169.1 mg, 95%).

(*E*)-2-(2-Iodo-1-phenylvinyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (6): Yellow oil; t_r 13.13; R_f 0.75 (hexane/EtOAc 9:1); IR ν 3040, 2981, 2922, 1490, 1441, 1357, 1318, 1209, 1137, 968, 851, 754, 697 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 1.39 (s, 12H), 6.98 (s, 1H), 7.27–7.30 (m, 5H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 25.1, 84.8, 87.3, 126.4, 127.7, 128.7, 142.2; ^{11}B NMR (160 MHz, $CDCl_3$) δ 30.40; MS *m/z* 356 (M^+, 100), 357 (M^++1, 16), 355 (22), 256 (12), 230 (11), 229 (68), 228 (15), 143 (32), 130 (10), 129 (52), 128 (23), 103 (18), 102 (16), 101 (30), 83 (44), 77 (22), 55 (11). Elemental analysis calcd. for $C_{14}H_{18}B_2IO_2$: C 47.23, H 5.10; Found: C 47.48, 5.25.

Chlorination and bromination of compound 2a. Typical procedure:[31] $CuCl_2$ (0.5 mmol, 67.2 mg) or $CuBr_2$ (0.5 mol, 112.2 mg) was added to a solution of the diboron compound **2a** (0.50 mmol, 178.0 mg) in THF (1.0 mL) and water (1.0 mL). After stirring for 1 h, the resulting mixture was extracted with EtOAc (20.0 mL) and the organic layer was dried over $MgSO_4$. After filtration and solvent evaporation, the residue was purified by column chromatography (basic alumina, hexane/EtOAc) to give the products **7** (88.4 mg, 62%) and **8** as yellow oils (150.9 mg, 98%).

(*E*)-2-(2-Chloro-1-phenylvinyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (7): Yellow oil; t_r 13.09; R_f 0.76 (hexane/EtOAc 9:1); IR ν 2982, 2925, 1491, 1444, 1359, 1320, 1209, 1142, 967, 851, 757, 698 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 1.37 (s, 12H), 6.73 (s, 1H), 7.22–7.33 (m, 5H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 24.9, 84.6, 126.9, 127.4, 127.6, 128.8, 138.9; ^{11}B NMR (160 MHz, $CDCl_3$) δ 30.68; MS *m/z* 266 (M^++2, 264), 265 (M^++1, 23), (M^+, 100), (33), 263 (25), 249 (18), 229 (53), 228 (18), 206 (13), 193 (19), 192 811), 191 (58), 190 (15), 187 (25), 186 (15), 185 (17), 166 (21), 165 (14), 164 (59), 163 (15), 149 (10), 147 (26), 144 (21), 143 (48), 129 (51), 128 (22), 103 (40), 102 (33), 85 (10), 77 (27), 59 (11) . Elemental analysis calcd. for $C_{14}H_{18}BClO_2$: C 63.56, H 6.86; Found: C 63.96, H 7.06.

(*E*)-2-(2-Bromo-1-phenylvinyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (8): Yellow oil; t_r 13.69; R_f 0.75 (hexane/EtOAc 9:1); IR ν 2976, 2927, 1490, 1441, 1364, 1319, 1211, 1138, 969, 851, 758, 727, 695 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 1.38 (s, 12H), 6.88 (s, 1H), 7.28–7.30 (m, 5H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 24.9, 84.7, 115.3, 126.7, 127.7, 128.8, 140.1; ^{11}B NMR (160 MHz, $CDCl_3$) δ 30.35; MS *m/z* 311 (M^++3, 12), 310 (M^++2, 78), 309 (M^++1, 30), 308 (M^+, 79), 293 (13), 237 (12), 235 (12), 229 (32), 210 (32), 209 (13), 208 (32), 187 (50), 186 (18), 185 (33), 171 (34), 170 (11), 144 (13), 143 (100), 130 (11), 129 (62), 128 (29), 128 (29), 103 (42), 102 (27), 85 (11), 77 (32), 59 (16). Elemental analysis calcd. for $C_{14}H_{18}BBrO_2$: C 54.42, H 5.87; Found: C 54.81, H 5.99.

Oxidation of compound 8: Following a literature procedure,[32] compound **9** was obtained in 70% yield. Compound **9** was characterized by comparison of its physical and spectroscopic data with those of an authentic commercial sample.

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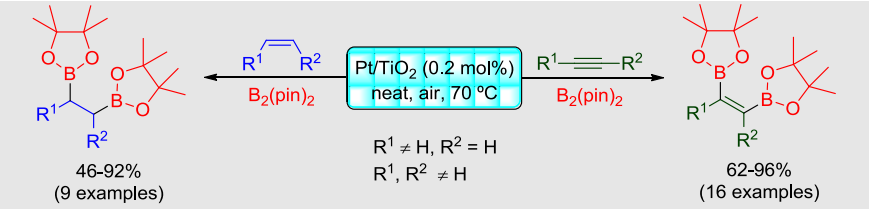

Click diboration: The diboration of alkynes and alkenes catalyzed by platinum nanoparticles on titania takes place under solvent- and ligand-free conditions in air.

The 1,2-diboronvinyl compounds have been obtained with exclusive *cis* stereochemistry and have been subjected to different useful chemical transformations.

Francisco Alonso, Yanina Moglie, Laura Pastor-Pérez, and Antonio Sepúlveda-Escribano**

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Solvent- and Ligand-free Diboration of Alkynes and Alkenes Catalyzed by Platinum Nanoparticles on Titania